

## Synthesis, Characterization and Dielectric Properties of Novel Metal Oxide - Phthalocyanine Nanocomposites

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ORGANIC and metal-organic polymers which have electrical properties have opened up a promising field in material science and engineering. Phthalocyanine ( $H_2Pc$ ) and metal oxide-phthalocyanine (MO-Pc) where (MO = ZnO, NiO, FeO and CoO) were prepared by urea fusion technique. The prepared composites were identified by means of Fourier transform infrared spectroscopy (IR) and X-ray diffraction (XRD). The XRD data indicate that the ZnO-Pc and NiO-Pc are highly crystalline and particle sizes are ranged from 28.4 to 57.2 nm and from 51.4 to 82.9 respectively. The dielectric properties including dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  of the prepared composites were calculated from the experimental capacitance values in the frequency range 100 Hz to 5MHz and in the temperature range of 25°C to 120°C. Generally,  $\epsilon'$  are found to be decreased with increasing frequency and increase with increasing temperature. It is obvious that, appearance of peak for each MO in the dielectric loss suggests the presence of relaxing dipoles in the MO-Pc nanocomposites. The relaxation time  $\tau$ , activation enthalpy  $\Delta H$  and the entropy change  $\Delta S$  of the prepared composites were calculated. The obtained data were correlated to the nature of doping metal oxide.

**Keywords:** Metal oxide-phthalocyanine, dielectric constant, dielectric loss and relaxation time.

### Introduction

In recent years, interest has been focused on the design of the smart and intelligent multifunctional nanomaterial as phthalocyanine (Pc) for technological applications. Phthalocyanines ( $H_2Pc$ ) are aromatic and chemically stable compounds containing four pyrrole units and it can be considered as a weak dibasic acid.  $H_2Pc$  has 18  $\pi$ -electron conjugated systems, in which different metal and non-metal ions can be included. A number of derivatives can be made in the macrocycle either by doping different central metal ions or by substitution of functional groups at the peripheral sites of the phthalocyanine ring. The metal atoms replace the two hydrogen atoms attached to the two isoindole group to form the highly stable metal phthalocyanines (M-Pc) with six membered chelate rings, through two covalent and two coordination bonds. Several research groups have focused on studying the various properties of organic semiconductor such as Metal-free  $H_2Pc$  and/or metal-substituted phthalocyanine compounds M-Pc. Their essential properties are attributed to their efficient electron

transfer abilities. It has dark colors so it is suitable for using Pc and its derivatives as dyes and pigments in textile industries[1].

On the other hand, the broad range of condensed phases, such as mono-crystals mesophases, Langmuir- Blodgett films etc.[2], has contributed to the progress of electronic and electrophotonic devices depend on these compounds[3]. So, phthalocyanine have a large industrial application related to intrinsic semiconductors as optoelectronic devices, solar cells, information storage systems, electronic imaging and liquid crystal display [4-10]. Pc derivatives as NiPc, CoPc and CuPc were used as gas sensing devices also; CuPc has been used in organic light emitting diodes [11, 12].

The photosensitive properties of phthalocyanine compounds were closely related to the particle size and the specific surface area. The potential and sensitivity of photoreceptors rose rapidly with the particle size of phthalocyanine reducing from micrometer scale to nanometer scale. Therefore, it is great significance to explore simple and effective

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methods for fabrications of nano-sized phthalocyanine. Preparation methods of nano-sized phthalocyanine mainly involve liquid phase direct reprecipitation, laser irradiation, mechanical grinding, gas condensation and sol-gel routes [13, 14]. Phthalocyanine particles synthesized by a sol gel method have a narrow particle size distribution and photoconductive performance. Nevertheless, it was reported that the synthesis of nano-sized titanium-oxophthalocyanine (TiO-Pc) was carried out separately with this method, and the processes were too complicated to be scaled up to commercial production [15].

In dielectric material the charges become polarized in applied alternating electric field such that the negative and positive charges move in opposite directions. Dipole orientation and ionic conduction interact strongly at microwave frequencies; generally at low frequency the nanocomposites have higher dielectric permittivity than microcomposites. The metal oxide (MO) nanoparticles are attractive because of their excellent physical and chemical properties. MO has high charge capacity, safety and low cost. So polymer composite consisting of the metal oxide nanocomposites shows good dielectric response as well as good stability [16].

The doping of inorganic nanofillers into polymer has resulted in polymer nanostructure materials have multi-functional, high performance composites. Little attention has been paid to study the nanometric structure of polyvinylidene fluoride (PVDF)-zinc oxide (ZnO) nanocomposites [17]. The metal oxide addition leads to the increase in dielectric permittivity of the PVDF which allow faster movement of the polymer chains and faster alignment of the dipoles.

In this work, metal free ( $H_2Pc$  phthalocyanine, and metal oxide - phthalocyanine) (MO-Pc) composites, where (MO = ZnO, FeO, CoO and NiO) were synthesized from the reaction of phthalic anhydride with metal nitrate by urea fusion technique. The characterizations of the prepared samples were carried out using XRD and IR-spectra. Finally the dielectric properties of the prepared composites were carried out through the measurement of dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  within the frequency range 100 Hz to 5 MHz and the temperature range from 20 °C to 120 °C. The thermodynamic parameters such as the activation enthalpies  $\Delta H$  and the entropy changes  $\Delta S$  of dielectric relaxation were calculated for the prepared *Egypt.J.Chem.* **61**, No.2 (2018)

composites from the usual rate equation.

## **Experimental**

### *Synthesis of $H_2Pc$*

The synthesis of Pc using phthalic anhydride as the precursor is a simple pathway by which Pc can be obtained with a high purity and recovery. 8.88 gm (0.06 mole) of phthalic anhydride was added to a 500 ml flask, followed by adding 30 gm of urea, 0.2 gm of ammonium molybdate as a reaction promoter. The temperature was gradually raised to 190-200 °C, and maintained for 4 hours with continuous stirring. The reaction product was cooled and boiled with distilled water many times. The precipitate was washed in sequence with 2 % HCl, dilute alkali, 25 % methanol and acetone. Final purification was done by drying the sample at 200 °C for 3 hours in a dry oven by which any traces of impurities were sublimed. A blue colored  $H_2Pc$  was obtained.

### *Synthesis of Metal oxide-Pc*

Cobalt, Nickel, Iron and Zinc oxide Phthalocyanine composites were prepared by the urea fusion technique in the dry method as follows: 8.88 gm (0.06 mole) of phthalic anhydride was added to a 500 ml flask, followed by adding 30 gm of urea, 0.2 gm of ammonium molybdate as a reaction promoter and 0.01 mole of metal nitrate  $MNiO_3$  where, M= Co, Ni, Fe and Zn. The same process of preparation and purification of MO-Pc were followed as mentioned above. Dark colored pigments of Pc were obtained with different colored ranged from blue to green powders.

### *Characterization*

FTIR confirms the presence of functional groups and XRD give information about the crystallinity and grain size of novel prepared composites.

### *FTIR-spectra*

FTIR-spectra of pure  $H_2Pc$  and the prepared metal oxide-Pc nanocomposites were recorded by using a Perkin Elmer model 1430 spectrophotometer at room temperature in the range 4000 – 400  $Cm^{-1}$  using KBr pellet technique.

### *X-ray Diffraction analysis*

Structural analysis was performed for the prepared composites using X- ray diffractograms provided with computer- controlled X-ray diffractometer formally made by PHILIPS-MPD X PERT equipped with Cu radiation  $CuK\alpha$  ( $K = 1.54056 \text{ \AA}$ ) the X pert diffractometer has

the Bragg - Brenano geometry. The X- ray tube used was a copper tube operating at 40 kV and 30 mA. The scanning range was 20 to 80 (2 h) with a step size of 0.02 (2 h) and counting times of 35/step. Quartz was used as the standard material to correct for the instrumental broadening.

X-ray powder diffraction (XRD) was performed at room temperature for predicting the crystal structure and calculating the particle size by using Scherer formula.

$$L = K \lambda / \beta \cos \theta \dots\dots\dots (1)$$

where k is the Scherer constant taken as 0.94,  $\lambda$  is the X-ray wavelength ( $\text{CuK}_\alpha = 0.15406 \text{ nm}$ ),  $\beta$  is the peak width of half-maximum, and  $\theta$  is the Bragg diffraction angle ranged from  $5^\circ \leq 2\theta \leq 80^\circ$ .

#### Transmission Electron Microscope Images

The transmission electron microscope (TEM) images were taken for the prepared metal oxides using a JEDL model 1230.

#### Dielectric Measurements

The dielectric properties (dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$ ) were measured as disc of 12 mm diameter and thickness of 2 mm were prepared by pressing powdered samples at 10 tons/cm<sup>2</sup> and subjected to temperature range from 25 °C to 120°C and frequency range from 100Hz to 5MHz using HI0KI 3532 LCR Hi-Tester. The dielectric constant  $\epsilon'$ , of the prepared H<sub>2</sub>Pc and MO-Pc composites were calculated from the measured capacitance according to the equation:

$$\epsilon' = C_p d / \epsilon_0 A \dots\dots\dots(2)$$

Where  $C_p$  is the measured capacitance, d is the thickness,  $\epsilon_0$  is the permittivity of free space equal to  $8.854 \times 10^{-12} \text{ F/m}$  and A is the effective area of the sample.

$$\epsilon'' = \epsilon' \tan \delta \dots\dots\dots(3)$$

The temperature dependence of  $\tau$  was determined through the application of the theory of rate processes to molecular dipole relaxation. The frequencies corresponding to the maximum energy loss  $F_m$  are used to calculate the relaxation times from the relation

$$\tau = 1 / 2\pi F_m \dots\dots\dots (4)$$

The activation enthalpies and the entropy changes of dielectric relaxation has been calculated from the usual rate equation

$$\text{Ln} (\text{T}\tau\text{K/h}) = 1/\text{T} (\Delta\text{H}_e/\text{R}) - (\Delta\text{S}_e/\text{R})\dots\dots\dots(5)$$

Here  $\Delta\text{H}_e$  and  $\Delta\text{S}_e$  are the enthalpy of activation and the entropy change per mole for dipole relaxation. Thus, from the slope of the plot of  $\text{Ln} (\text{T}\tau\text{K/h})$  against  $1/\text{T}$ ,  $\Delta\text{H}_e$  can be obtained where  $\Delta\text{S}_e$  obtained from the intercept of this representation.

## Results and Discussion

### Characterization of Phthalocyanine Composites

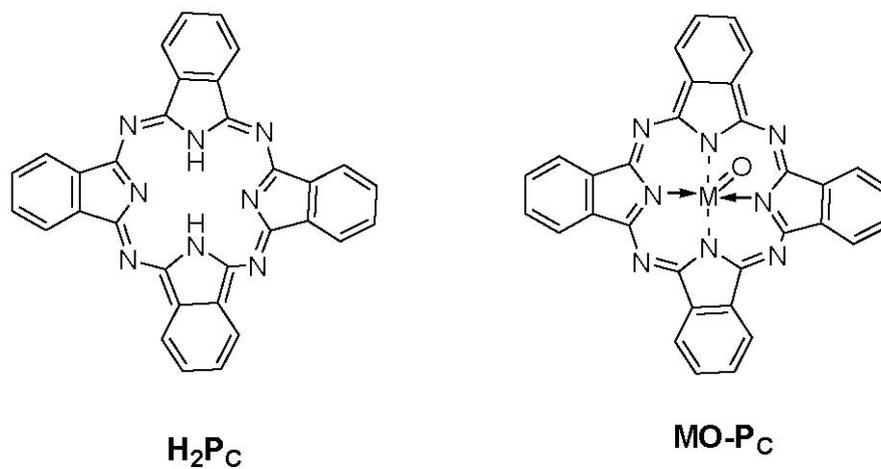
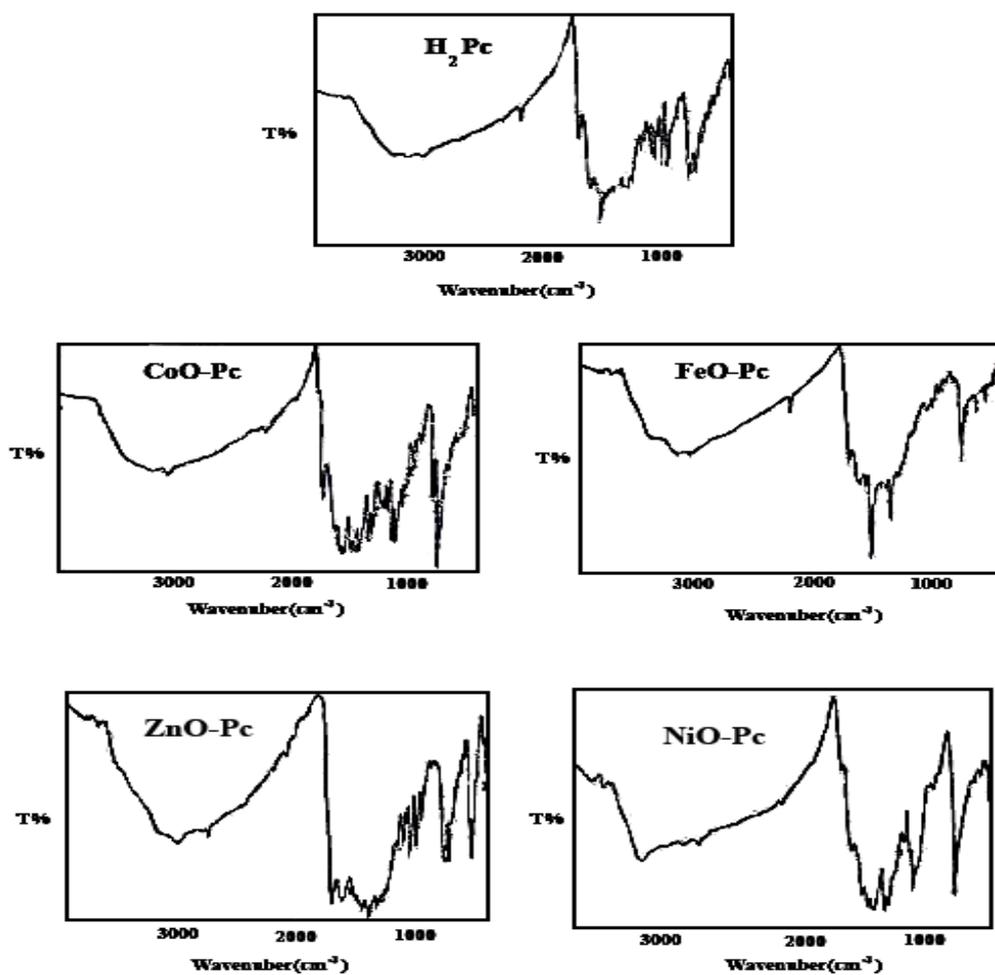
We are succeeded in the preparation of metal free Pc (H<sub>2</sub>Pc) and its stable nano-phthalocyanine metal oxide composites (CoO-Pc, FeO-Pc, NiO-Pc and ZnO-Pc) by urea fusion technique. The composition and the structure of the prepared phthalocyanine composites as shown in Scheme 1 identified by IR- TEM images and XRD analysis.

### IR-Spectra

FTIR spectra were recorded for both the H<sub>2</sub>Pc and its MO-Pc composites in the range of 400-4000 cm<sup>-1</sup>. The spectra are shown in Fig. 1. IR spectra of H<sub>2</sub>Pc exhibit a peak at 3431 cm<sup>-1</sup> attributed to N-H stretching vibration peak and the peaks around 1719 cm<sup>-1</sup> can be correlated with C=N stretching vibration[18]. The strong peak at 740 cm<sup>-1</sup> and 1110 cm<sup>-1</sup> are considered to be associated with the N-H out of plane and in plane deformation respectively. The broad band observed at around 3200 cm<sup>-1</sup> was assigned to CH<sub>2</sub> stretching vibration. Broad peak of CH group at 1590 cm<sup>-1</sup> and strong peak pointed for presence of C- C stretching vibration of phenyl ring around 2360 cm<sup>-1</sup>[19]. The peaks of MO-Pc spectra assigned at around 680 cm<sup>-1</sup> shift towards lower wavenumber, due to the strong interaction of metal oxide with nitrogen atom in Pc to form a coordination bond. The observed frequencies of metal free phthalocyanine and its nano metal oxides composites are listed in Table 1.

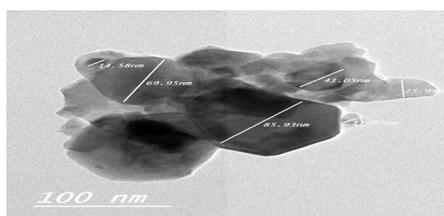
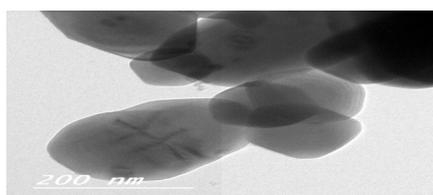
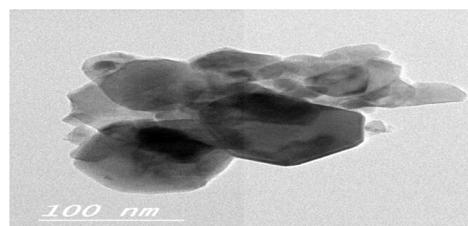
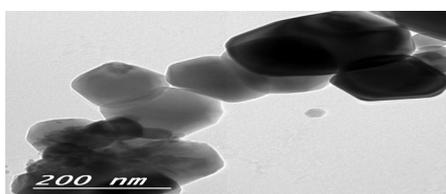
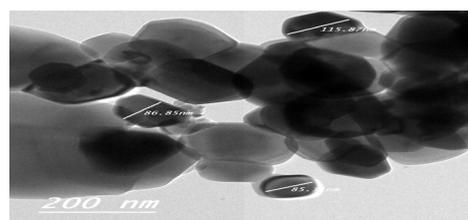
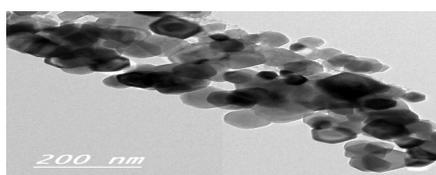
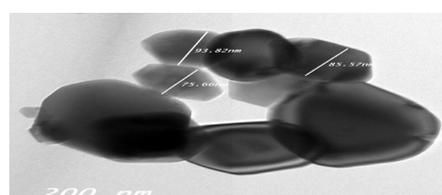
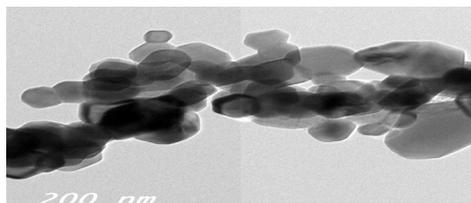
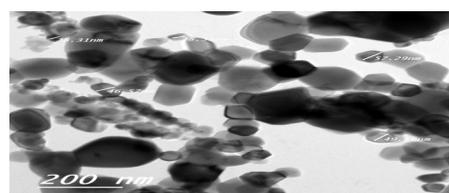
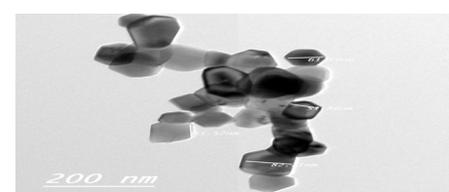
### TEM images of prepared nano metal oxides – Pc composites

The nano- metal oxides-Pc composites are investigated by transmission electron microscope and its results are shown in Fig. 2. From TEM images, all the prepared composites are in the nano scale and show definite crystal shape with 75–82 nm size range.

Scheme 1. H<sub>2</sub>P<sub>c</sub> and MO-P<sub>c</sub>Fig.1. IR spectra of H<sub>2</sub>P<sub>c</sub> and MO-P<sub>c</sub>.

**TABLE 1. Infra-Red Spectra of H<sub>2</sub>Pc and the prepared MO-Pc nanocomposites.**

	H <sub>2</sub> Pc	FeO-Pc	CoO-Pc	NiO-Pc	ZnO-Pc
C-N	1298-1257	1294-1362	1160-1285	1285	1399
C=N	1719	1717-2219	1720-1767	1707	1615
Conjugated system	1009-1062-1113-1131	1059-1089-1190	1010-1032-1120	1080-114-1160	1088-1117
CH	771-726-711	717-764	776-754-727	719	722
C=C	1393-1441-1471	1401-1439-1523	1397-1426-1450	1322-1422-1464	1399-1460
-CH aromatic	955-834	854-904-960	943-912-808	944-909	885

**H<sub>2</sub>Pc****CoO-Pc****FeO-Pc****ZnO-Pc****NiO-Pc****Fig. 2. TEM of H<sub>2</sub>Pc and its nano metal oxide composites**

### *X-Ray Diffraction studies*

The X-ray powder diffraction pattern of H<sub>2</sub>Pc and its metaloxo-PC (ZnO-Pc, FeO-Pc, NiO-Pc and CoO-Pc) has been studied at room temperature. The data of  $d$  (Å) values,  $2\theta$  and the crystal size of the prepared composites are given in Table 2 and are graphically represented in Fig. 3. The XRD pattern of H<sub>2</sub>Pc showed one broad peak with high intensity from 10° to 20° and another broad one with low intensity from 20° to 35° which indicates the formation of MF - PC with low crystalline nature.

On the other hand the XRD patterns for the MO-Pc are rich with high and medium intensity peaks in the range of 4°–80° besides the two broad bands observed for MF-Pc. The presence of this high and medium intensity peaks ensure the presence of the metal oxide as separate phase in the matrix of the conjugated phthalocyanine composites expect for FeO -Pc and CoO -Pc composites where the characteristic peaks are broad and less intense, indicating that the iron oxide and cobalt oxide supports crystals to grow which can be attributed to its encapsulation by phthalocyanine and the ability of these metal oxides to form amorphous metal (some authors called them bulk metallic glass) [20] as a result of their high magnetic character of Fe<sup>2+</sup> and Co<sup>2+</sup>, where Fe<sup>2+</sup> has 4 unpaired electrons occupied 3d orbital and has a magnetic moment equal to 5.1 – 5.7  $\mu$ B and Co<sup>2+</sup> has 3 unpaired electrons occupied 3d orbital and has a magnetic moment equal to 4.2 – 4.8  $\mu$ B [21 - 23].

For Pure ZnO powder there are sharp peaks at 31.837°, 34.502°, 36.334°, 47.650°, 56.726°, 63.012° and 68.114° corresponding to diffraction planes and  $d$  value of 2.8112 (100), 2.5996 (002), 2.4702 (101), 1.9092 (102), 1.6239 (110), 1.4763 (103), 1.4060 (200), 1.3777 (112) and 1.3590 (201) are observed and they are in accordance with the ZnO structure (Reference pattern JCPDS 5-0664). As shown in Fig. 2, these peaks are observed in XRD pattern of ZnO-Pc composite and extra peak at 15.3° of Pc which indicates the presence of ZnO in Pc and no peaks of impurity were observed suggesting that the high purity ZnO-Pc was obtained [18, 22]. We also found that XRD pattern of NiO-Pc is the same pattern of NiO (Reference pattern JCPDS No. 04-0835) and extra peak characteristic for the presence of phthalocyanine. Referring to Table 2, we found the crystal size of ZnO-Pc ranged from 28.4 nm to 57.2 nm, for NiO-Pc ranged from 51.1 nm to

82.1 nm while it ranges from 85 – 115.2 nm for CoO -Pc [24,25]. these values matches well with that obtained from TEM images.

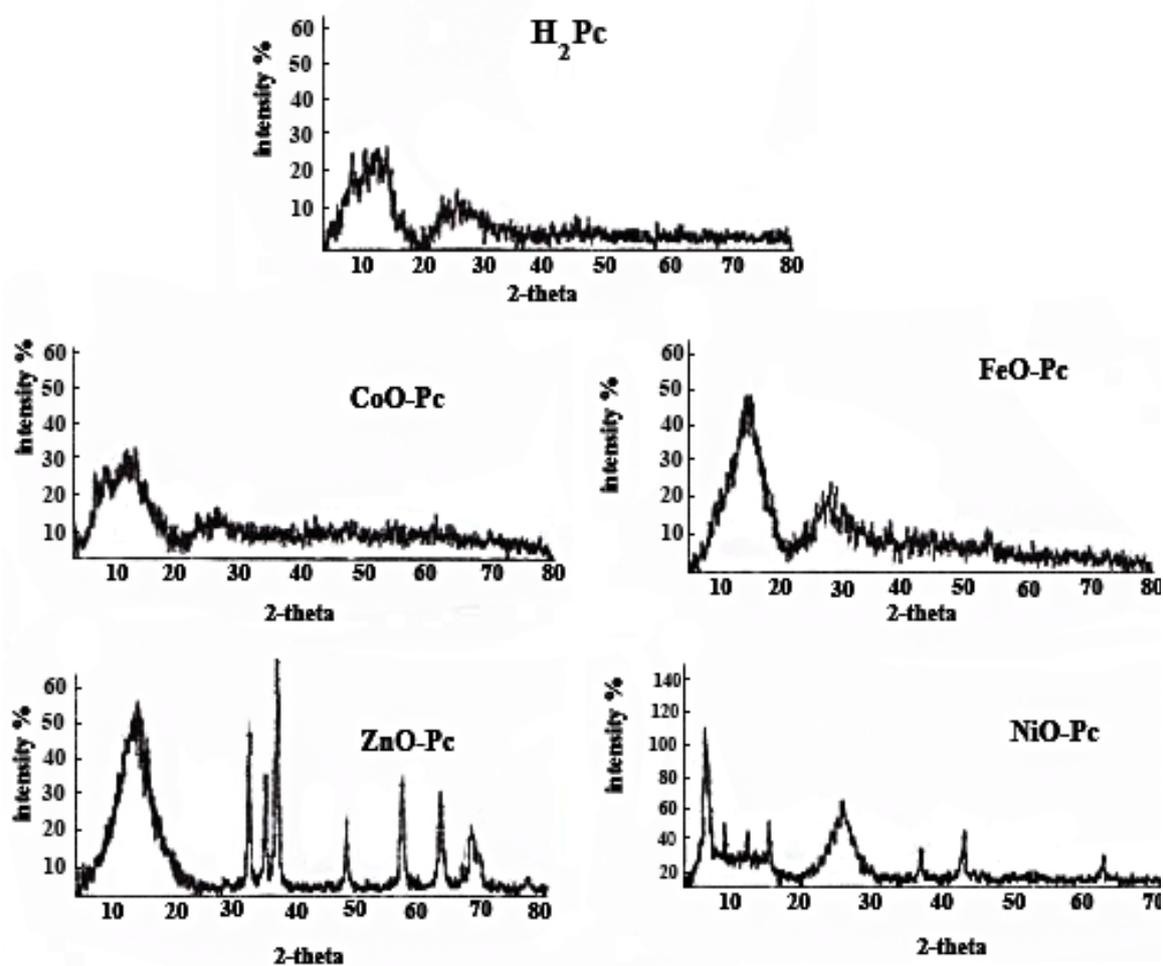
### *Dielectric properties*

In general, the conjugated organic polymer is insulating or sometimes semiconductors. Electrons cannot move along polymers chain because of the lack of charged carriers and also the different bond lengths along the polymer chain. To make these polymers conductive, mobile charge carriers (doping) must be introduced by a series of oxidations or reductions, that similar to the changes that occurs in the electrical properties of inorganic semiconductor [26].

Electrical study of composites by measuring dielectric properties at different temperatures and frequency is one of the most important characters to investigate their use in electrical devices. Basically, dielectric constant  $\epsilon'$  is the measure of how easily a material is polarized in the presence of external electric field. for heterogeneous dielectric materials the changes in the value of  $\epsilon$  as a function of frequency are attributed to the space charges polarization (Maxwell- Wagner-Sillar) owing to moving of free charges at the interfaces of the composites and dielectric relaxation due to segmental movement [27,28]. When measuring the dielectric constant of composites at different frequencies, by applied electric field, the energies of the dipoles situated on each side of the potential barrier will be changed such that, the dipoles parallel to the field have lower potential energy than those anti-parallel to the field. The dipoles will perform oscillation at a resonance frequency about their equilibrium position and their transition from one position to another will be associated with the possibility of rotation.

Figure 4 shows the variation of  $\epsilon'$  with frequency ranged from 100 Hz to 5 MHz at different temperatures ranged from 20°C to 120°C for H<sub>2</sub>Pc and its metal oxide composites. For all sample under study it is obvious that, the  $\epsilon'$  have a high value then decrease with increasing the frequency reached a low value independent on frequency at higher one. Similar behaviors have been obtained for CuPc, ZnPc and CoPc as previously reported for Pc metal composites [29, 30].

At lower frequencies dielectric constant  $\epsilon'$

Fig. 3. XRD spectra of H<sub>2</sub>Pc and MO-Pc composites.TABLE 2. X-ray diffraction data ( $2\theta$ , d-spacing and intensity of the prepared MO-Pc nanocomposites.

CoO-Pc			NiO-Pc			ZnO-Pc		
$2\theta$	D-spacing (Å)	grain size(nm)	$2\theta$	d-spacing (Å)	grain size(nm)	$2\theta$	d-spacing (Å)	grain size(nm)
6.99	12.62	86.8	6.86	12.88	51.5	31.72	2.82	28.4
8.79	10.05	85.7	9.57	9.24	60.2	34.38	2.61	49.2
25.93	3.08	88.8	12.75	6.94	62.5	36.19	2.48	28.3
29.94	2.98	115.2	15.79	5.61	60.3	47.47	1.91	52.2
			26.13	3.41	51.1	56.54	51.5	50.4
			37.17	2.42	55.5	62.81	55.5	40.2
			43.25	2.09	61.3	66.30	61.3	55.3
			62.88	1.48	82.1	67.77	82.1	37.1
						69.09	1.35	49.1
						76.87	1.24	57.2

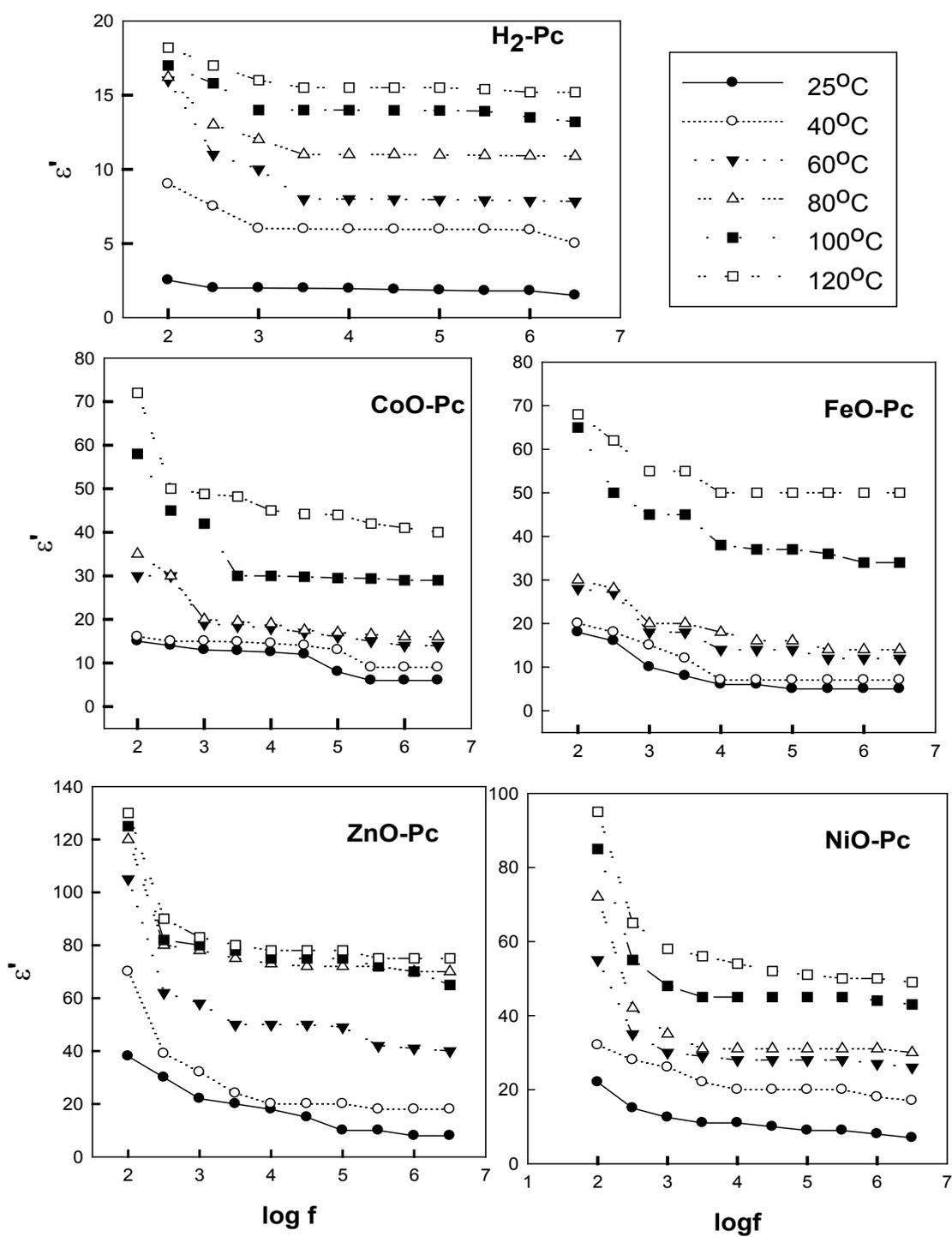


Fig.4. Variation of dielectric constant  $\epsilon'$  with frequency at different temperatures for H2Pc and MO-Pc.

of  $H_2Pc$  has a high value due to the presence of four polarizations (space charge, orientation, electronic, and ionic polarization). As the frequency increases, the larger dipolar groups find it difficult to orient hence  $\epsilon'$  decreases and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually.

Similarly, MO-Pc have high value of  $\epsilon'$  at low frequencies reveals that the system exhibits strong interfacial polarization (IP) between metal oxides and phthalocyanine. IP occurs when there is an accumulation of charge at interface within the material when electric field is applied. This interfacial polarization is particularly dominant at low frequencies and in conjugated polymers. MO displays strong Ionic polarization due to  $M^{2+}$  and  $O^{2-}$  ions thus has a high permittivity value [31, 32]. The dielectric of MO-Pc nanocomposites decrease with increasing frequency due to the variation in the applied electric field is very rapid for the dipoles to align themselves. One can note from Fig. 4, that, at definite temperature as  $120^\circ\text{C}$  and with increasing frequency from 100Hz to 5MHz the obtained data for dielectric constant decreased from 18 to 15 for  $H_2Pc$ , from 130 to 75 for ZnO-PC, from 95 to 49 for NiO-Pc, from 72 to 40 for CoO-Pc and for FeO-Pc decrease from 68 to 50.

To understand the effect of temperature on electrical response of composite we studied the variation of dielectric constant with temperature at definite frequencies as shown in Fig. 5. At lower temperature, as the dipoles are rigidly fixed in the dielectric, the field cannot change the condition of dipoles. But on increasing the temperature the dipoles somewhat become free and they reply to the applied electric field [33] enhancing the ease of the orientation polarization of polar groups and polar bonds such as (O-M bonds and M-N bonds) [34]. So the effect of neighboring atoms or molecules decreases with increasing temperature, hence dielectric permittivity is also increased with the temperature.

Figure 6 represents the variation of  $\epsilon'$  of  $H_2Pc$  and MO-Pc at temperature at 1 KHz, it is obvious that, the dielectric constant  $\epsilon'$  obtained for  $H_2Pc$  increases slowly at all temperature range. Dielectric constant  $\epsilon'$  of MO-Pc composites increase slowly from  $20^\circ\text{C}$  to  $80^\circ\text{C}$  then fast increase from  $80^\circ\text{C}$  to  $120^\circ\text{C}$ . The value of  $\epsilon'$  for  $H_2Pc$  was varied from 2.2 to 16.1 and that recorded for FeO-Pc, CoO-Pc, NiO-Pc, and ZnO-Pc were

varied from 8.1 to 55.3, from 13.2 to 55.6, from 14.3 to 60.4, and from 22.1 to 83.3 respectively. The increase in  $\epsilon'$  values with different metal oxide may be due to change in the free volume as we have different metals with different atomic radii as well as the magnitude of dipole-dipole interaction and segmental mobility. Moreover, the recorded high values of  $\epsilon'$  for ZnO-PC followed by NiO-Pc. The high values of dielectric constant  $\epsilon'$  recorded for ZnO-Pc is a result of high polarization [35], also ZnO-Pc and NiO-Pc have high crystalline structure and nano size range as explained earlier in XRD spectral analysis.

Figure 7 shows the variation of dielectric loss  $\epsilon''$  with frequency at different temperatures, For all the prepared MO-Pc composites the dielectric absorption bands appear suggests the presence of relaxing dipoles in the prepared nanocomposites. Generally, the calculated  $\epsilon''$  spectrum contains contribution from two sources: dipolar orientation of polar groups and diffusion of free charge carrier and its trapping in the holes. When interfacial polarization occurs it can be written as

$$\epsilon''_{mean} = \epsilon''_D + \epsilon''_{dc} + \epsilon''_{ip} \dots \dots \dots (6)$$

Where  $\epsilon''_D$  is orientation polarization (Debye type),  $\epsilon''_{dc}$  is DC conduction and  $\epsilon''_{ip}$  is interfacial polarization [36].

Dielectric loss decreases with increasing frequency above the critical frequency  $F_m$  related to highest energy loss more than that required for activation and also with increasing temperature  $\epsilon''$  decreases so relaxation peak shifts towards higher frequency side suggesting the speed up of the relaxation time [37].

The various relaxation processes can be classified as  $\alpha$ - and  $\beta$ - relaxation. The  $\alpha$ -relaxation is mainly existing in an extremely crystallized polymer and is attributed to the movement of the main chain in the crystalline phase, while in  $\beta$ - relaxation is due to amorphous part in amorphous materials. When measuring the dielectric properties of organic samples at different frequencies, by an applied electric field, the energies of the dipoles situated on each side of the potential barrier will be changed such that, the dipoles parallel to the field have lower potential energy than those anti-parallel to the field. The dipoles will perform oscillation at a resonance frequency about their equilibrium position and their transition from one position

to another will be associated with the possibility of rotation. So the rotational polarization plays a significant role in dielectric relaxation. One can conclude that the relaxation time depends on temperature. The rotation of the dipoles associated with jumping over the potential barriers, hindering rotation can be taken as a model to describe the dielectric relaxation as well as the relaxation process caused by the restricted motion of the side groups at relatively low temperature. It is reasonable to conclude that the relaxation occurring in such composites is  $\beta$ -relaxation originated mainly from lattices defects due to metal oxide ionization and electron transfer which lead to charged centers or polar bonds and groups or sites possessing polarization.

The frequency corresponding to maximum

energy loss  $F_m$  is used to calculate the relaxation time as equation (4) and hence activation enthalpies  $\Delta H$  and the entropy  $\Delta S$  from the relation (5) can be calculated. The calculated data are listed in Table 3. This table shows that the relaxation time decreases with increasing the temperatures for every sample explained above. The value of the enthalpy changes of the dielectric relaxation, which ranged from  $11 \times 10^3$  KJ/mole for  $H_2Pc$  to  $18.5 \times 10^3$  KJ/mole for  $ZnO-Pc$ , which is in a good agreement with the previous definition of  $\beta$  relaxation. The values of the entropy changes of dielectric relaxation  $\Delta S$  were the same also listed in Table 3, it can be seen that the values of  $\Delta S$  are all negative with low values, which means that the rate determining factor in the relaxation process includes the displacement of the free charges.

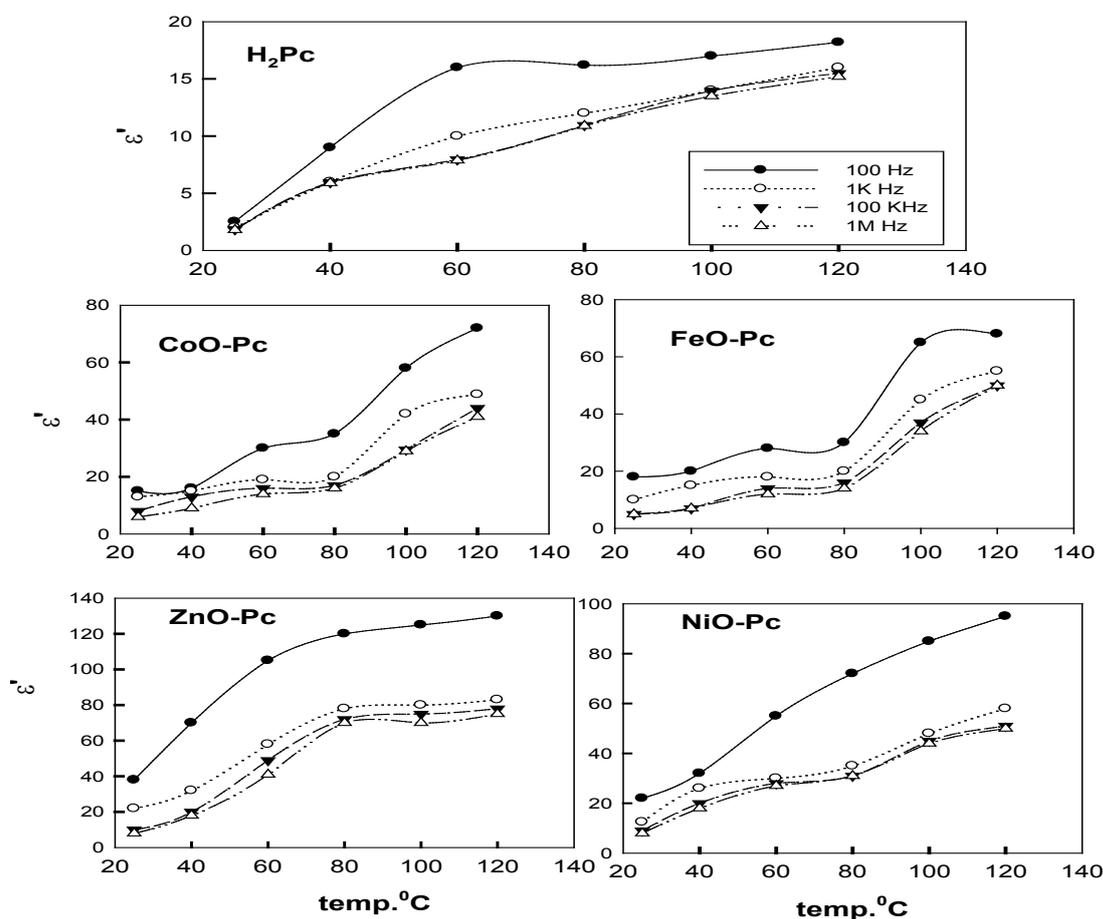


Fig.5.Variation of dielectric constant  $\epsilon'$  with temperature at different frequencies for  $H_2Pc$  and different  $MO-Pc$ .

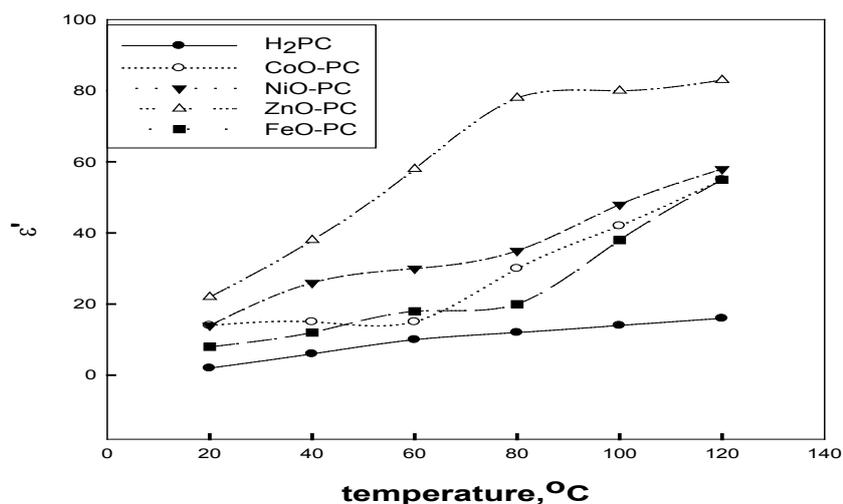


Fig.6.Variation of dielectric constant with temperature at 1000Hz for H<sub>2</sub>Pc and MO-Pc.

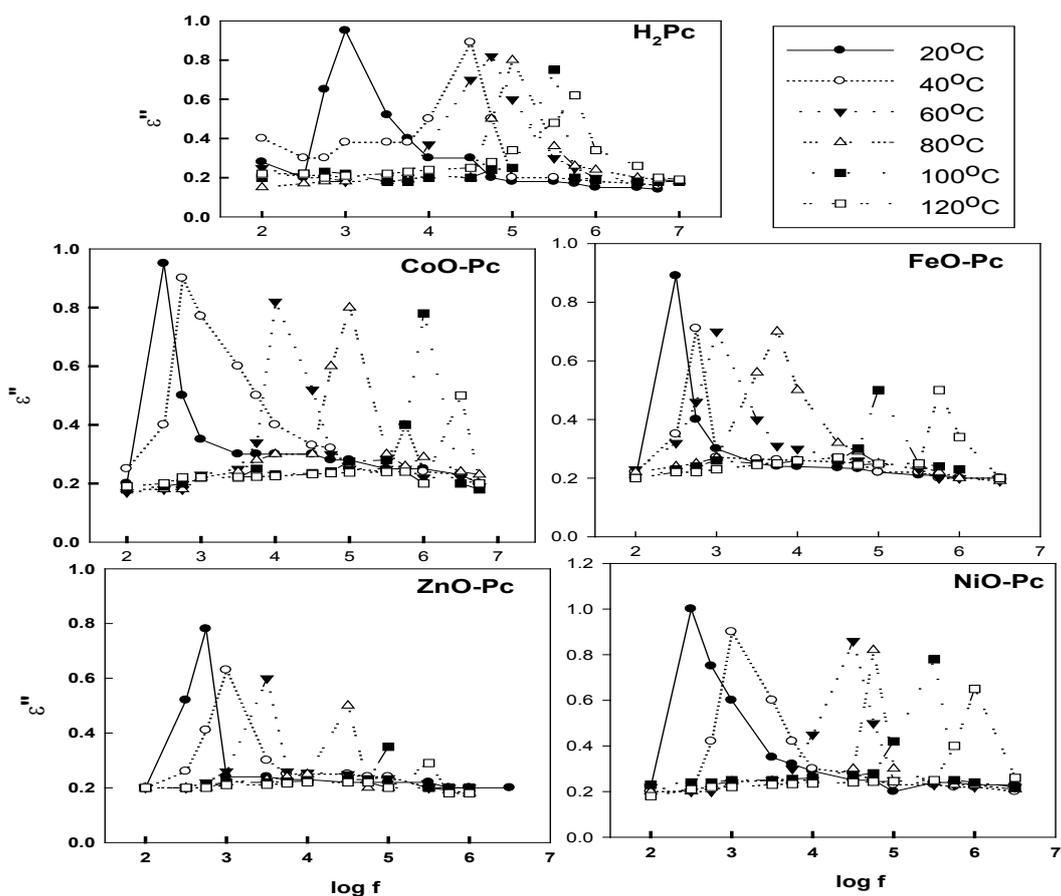


Fig.7. Variation of dielectric loss  $\epsilon''$  with frequency at different temperature for H<sub>2</sub>Pc and MO-Pc.

**TABLE 3.** The relaxation time, Activation enthalpies  $\Delta H$  and the entropy changes  $\Delta S$  of the prepared MO-Pc composites.

Prepared samples MO-Pc	$\tau$ (sec)						$\Delta H$ KJ/mole	$\Delta S$ J/deg/mole
	20°C	40°C	60°C	80°C	100°C	120°C		
H <sub>2</sub> Pc	1.76x10 <sup>-4</sup>	3.19x10 <sup>-6</sup>	1.59x10 <sup>-6</sup>	5.31x10 <sup>-7</sup>	2.28x10 <sup>-7</sup>	3.19x10 <sup>-7</sup>	11.69x10 <sup>3</sup>	0.52
CoO-Pc	2.27x10 <sup>-4</sup>	1.59x10 <sup>-4</sup>	5.31x10 <sup>-7</sup>	2.27x10 <sup>-7</sup>	1.17x10 <sup>-7</sup>	7.96x10 <sup>-8</sup>	16.19x10 <sup>3</sup>	-10.43
FeO-Pc	5.3x10 <sup>-4</sup>	3.2x10 <sup>-4</sup>	1.8x10 <sup>-4</sup>	1.6x10 <sup>-4</sup>	1.59x10 <sup>-6</sup>	3.19x10 <sup>-7</sup>	17.52x10 <sup>3</sup>	-12.05
NiO-Pc	1.77x10 <sup>-4</sup>	1.59x10 <sup>-4</sup>	5.31x10 <sup>-7</sup>	3.18x10 <sup>-7</sup>	2.27x10 <sup>-7</sup>	1.77x10 <sup>-7</sup>	14.65x10 <sup>3</sup>	-7.42
ZnO-Pc	5.3x10 <sup>-4</sup>	2.3x10 <sup>-4</sup>	1.59x10 <sup>-4</sup>	1.59x10 <sup>-6</sup>	1.77x10 <sup>-7</sup>	3.19x10 <sup>-7</sup>	18.49x10 <sup>3</sup>	-10.93

### Conclusion

Phthalocyanine H<sub>2</sub>Pc, and metal oxide-phthalocyanine MO-Pc (where MO = FeO, CoO, NiO and ZnO) were prepared by urea fusion technique in the dry method. IR-spectra and diffraction X-ray analysis were done on the prepared composites to confirm their structure. XRD studies confirm the crystalline phase of MO-Pc in order ZnO-Pc > NiO-Pc > CoO-Pc > FeO-Pc. The crystal-linty increased particle size of ZnO-Pc is ranged from 28.4 nm to 57.2 nm where it ranged from 51.4 to 82.4 nm for NiO-Pc

From the dielectric studies, it was concluded that the dielectric constant  $\epsilon'$  is frequency and temperature dependent within the used ranges. The dependent of  $\epsilon'$  values on metal oxide doping may be attributed to change in the free volume because we have different metal oxides with different atomic radii as well as the magnitude of dipole-dipole interaction and the segmental mobility.

The dielectric loss  $\epsilon''$  curves have an absorption maximum corresponding to the relaxation times. From the values of  $\Delta H$ , it is reasonable to conclude that the relaxation occurring in such composites is  $\beta$ -relaxation originated from lattices defects due to ionization of metal oxide and transfer of electron which lead to charged centers and polar bonds M-O and M-N. Relaxation times become shorter as the temperature increased indicates high availability of free charges.

The very low value of dielectric constant  $\epsilon'$  at higher frequencies is important for the fabrication of materials towards ferroelectric, photonic and

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electrooptic devices

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### تشديد وتوصيف وخواص العزل الكهربائي لمترابكات نانومترية جديدة للفيثالوسيانين مع الاكاسيد الفلزية

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فتحت البوليمرات العضوية والفلزية العضوية التي لها خصائص كهربائية مجالا واعدا في علم المواد والهندسة. وقد تم تحضير مركب الفيثالوسيانين ومترابكات أكسيد الفلز للفيثالوسيانين الجديدة (أكسيد الفلز= أكسيد الزنك وأكسيد النيكل وأكسيد الكوبالت وأكسيد الحديد) بواسطة تقنية انصهار البوريا.

ولقد تم اثبات تركيب هذه المركبات التي تم تحضيرها عن طريق طيف الأشعة تحت الحمراء والميكروسكوب الالكتروني الماسح وحيود الأشعة السينية. وتشير الدراسات ان مترابكات اكسيد الزنك والنيكل للفيثالوسيانين – هي مترابكات بلورية نانومترية وحجم الجسيمات يتراوح بين ٤, ٢٨ الي ٢, ٥٧ نانومتر لمترابكات الزنك وبينما تراوحت بين ٨٥ الي ١١٥ نانومتر لمترابكات النيكل على التوالي.

تم دراسته الخصائص العازلة بما في ذلك ثابت العزل وفقدان العزل للمركبات المحضرة في مدي الترددات ١٠٠ هرتز إلى ٥ ميغا هيرتز وفي مدي درجات الحرارة ٢٥ درجة مئوية إلى ١٢٠ درجة مئوية. وقد وجد ان ثابت العزل ينخفض مع زيادة التردد ويزيد مع زيادة درجة الحرارة.

ومن الواضح ظهور ذروة للاسترخاء لكل مترابكات عند دراسة معامل الفقد الكهربائي. وتم حساب وقت الاسترخاء ومنه تم حساب الإنثالبي والانتروبي للمركبات المحضرة.

ومن النتائج التي تم الحصول عليها نجد ان هناك ارتباط بين الخواص الكهربائية مع طبيعة أكاسيد الفلزات المختلفة الداخلة في التركيب.